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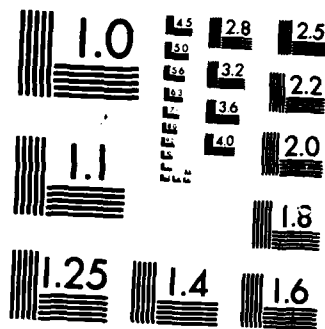
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Annual Technical Summary Report

AD-A165 706

InP Materials

30 September 1985

Lincoln Laboratory

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

LEXINGTON, MASSACHUSETTS



Prepared for the Department of the Air Force
under Electronic Systems Division Contract F19628-85-C-0002.

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The work reported in this document was performed at Lincoln Laboratory, a center for research operated by Massachusetts Institute of Technology, with the support of the Department of the Air Force under Contract F19622-85-C-0002. A part of this support was provided by the Rome Air Development Center.

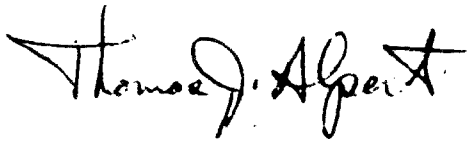
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The ESD Public Affairs Office has reviewed this report, and it is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER

A handwritten signature in black ink, reading "Thomas J. Alpert". The signature is stylized with a large, sweeping initial "T" and a star-like flourish at the end.

Thomas J. Alpert, Major, USAF
Chief, ESD Lincoln Laboratory Project Office

**MASSACHUSETTS INSTITUTE OF TECHNOLOGY
LINCOLN LABORATORY**

InP MATERIALS

**ANNUAL TECHNICAL SUMMARY REPORT
TO THE
ROME AIR DEVELOPMENT CENTER**

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1 OCTOBER 1984 — 30 SEPTEMBER 1985

ISSUED 22 JANUARY 1986

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ABSTRACT

This report covers the work on InP materials carried out with the support of the Department of the Air Force during the period 1 October 1984 through 30 September 1985. A part of this support was provided by the Rome Air Development Center. The current objectives of the program are to improve the yield of high-purity polycrystalline InP used as source material for crystal growth, to optimize the liquid-encapsulated Czochralski (LEC) method in order to grow single crystals with low defect density, low residual impurity concentration and uniform dopant concentration, and to investigate dopants that might yield semi-insulating InP with improved thermal stability.

Electrical measurements were made on samples from 22 of the 30 polycrystalline InP ingots synthesized. None had mobilities exceeding $5 \times 10^4 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. The decrease in the yield of high-purity ingots compared to previous years can be attributed to the low purity of as-received P and the ineffectiveness of P prebaking. We believe that Si continues to be the dominant donor impurity in the less pure ingots.

For almost all the LEC InP boules in previous years the growth axis was in a $\langle 111 \rangle$ direction. We have initiated experiments to determine the conditions necessary for twin-free LEC growth of $\langle 100 \rangle$ crystals. In a series of paired $\langle 100 \rangle$ and $[111\text{B}]$ growth runs, twinning was much more probable for $\langle 100 \rangle$ growth. To achieve a high yield of twin-free $\langle 100 \rangle$ crystals it will apparently be necessary to use larger temperature gradients than those sufficient to obtain twin-free $[111\text{B}]$ crystals.

We are developing a technique for obtaining better estimates of the residual impurity concentration in semi-insulating Fe-doped InP. For this purpose we are utilizing low-temperature measurements of the optical absorption in the vicinity of 3.5 μ m that is associated with intra-atomic transitions of the Fe²⁺ compensated acceptor. This absorption is proportional to the concentration of occupied Fe acceptor levels, which is equal to the net shallow donor concentration. After an accurate value of the absorption cross section is determined, we plan to use this technique for routine characterization of semi-insulating substrates.

An investigation of the effect of V doping on the electrical and optical properties of n- and p-type InP has shown that V behaves as a very deep donor located -0.2 eV above the valence band. Therefore InP cannot be made semi-insulating by V doping.

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INTRODUCTION

The goals of the InP materials program at Lincoln Laboratory are the development of reliable techniques for preparing high-quality InP crystals with controlled electrical properties and the utilization of these techniques to produce crystals needed for research on optoelectronic devices such as InP photoconductive switches and GaInAsP/InP diode lasers and detectors and on electronic devices such as JFETs.

Our program consists of two parts: synthesis of InP from the elements and crystal growth by the liquid-encapsulated Czochralski (LEC) method. Synthesis is carried out in order to assure an adequate supply of charge material with the purity desired for LEC growth, since such material is not consistently available from commercial sources.

In this report we first review the results of synthesis runs performed during FY85. We then discuss the following topics: LEC growth of <100>-oriented InP boules, initial development of a technique for utilizing low-temperature optical absorption measurements to determine the net shallow donor concentration in semi-insulating Fe-doped InP crystals, and electrical and optical measurements showing that V in InP behaves as a very deep donor located -0.2 eV above the valence band.

SYNTHESIS OF POLYCRYSTALLINE INGOTS

Synthesis of InP from the elements was carried out in horizontal fused silica boats sealed inside fused silica ampoules as described in the report for FY81. Thirty polycrystalline ingots, each weighing about 1 kg,

were synthesized during FY85. All of the ingots were solidified at temperatures between 1050 and 1060°C, with P reservoir temperatures ranging from 460 to 470°C. As in previous years, Hall coefficient (R_H) and resistivity (ρ) measurements were made when the grain size was large enough to permit rectangular single-crystal bars at least $1 \times 2 \times 10 \text{ mm}^3$ to be cut out. All of the samples were n type. The electron concentration at 300 K (n_{300}) was calculated from $n = -e^{-1} R_H^{-1}$, and the Hall mobility at 77 K (μ_{77}) from $\mu = R_H \rho^{-1}$.

Table I lists in chronological order each of the 22 ingots synthesized in FY85 for which electrical measurements could be made, together with the lots of In and P used and the values of n_{300} and μ_{77} for a sample cut from near the first-to-freeze end of the ingot. The distributions of the μ_{77} values measured for samples from FY80 through FY85 are shown in histogram form in Fig. 1. From this figure it is evident that the reduction in the yield of high-purity ingots noted in the last two reports became even more severe during the past year, since no ingots with $\mu_{77} > 5 \times 10^4 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ were prepared in FY85, whereas the fraction of such ingots was 2/12 in FY84, 7/20 in FY83 and 23/44 for FY80 through FY82. Furthermore, for all the FY84 and 85 ingots and most of the FY83 ingots the P was vacuum baked in the synthesis ampoule before InP synthesis, while P prebaking was not used for any of the FY80-82 ingots.

In the report for FY83 we suggested that the reduction in the yield of high-purity ingots resulted from a decrease in the purity of the P used as starting material. In the report for FY84 we attributed the further

Table I. Synthesis Parameters and Electrical Properties of InP Ingots

Ingot	Indium		Phosphorus		InP	
	Source, lot	Vac. bake (°C, h)	Source, lot	Vac. bake (°C, h)	n_{300}^{16} (10^{16} cm^{-3})	μ_{77}^{27} ($10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
1	ICA, 595	900, 6	MCP, 7403	216, 5	1.1	2.1
2	ICA, 595	900, 6	RASA, 4093	200, 60	7.3	0.56
3	ICA, 595	900, 6	MCP, 8401	240, 2	0.49	2.5
4	ICA, 804	900, 6	MCP, 8307	225, 4	1.7	1.4
5	ICA, 804	900, 6	MCP, 8307	20, 24	1.0	2.2
6	ICA, 843	900, 6	JM, 70168	240, 60	0.17	4.5
7	ICA, 843	900, 6	JM, 70168	350, 24	9.9	0.50
8	ICA, 843	900, 6	MCP, 8402	300, 8	6.3	0.62
9	UMC, 9427	850, 12	UMC, 41128	360, 70	5.7	0.63
10	UMC, 9427	820, 12	UMC, 41128	300, 3	3.6	1.0
11	ICA, 118	750, 12	MCP, 8402	220, 6	1.8	1.2
12	ICA, 804	700, 12	MCP, 8402	220, 4	1.9	1.0
13	ICA, 804	700, 12	MCP, 8402	290, 4	1.0	1.7
14	ICA, 849	825, 6	MCP, 8404	290, 30	2.5	1.2
15	ICA, 849	825, 6	MCP, 8404	300, 2	3.6	1.0
16	ICA, 849	825, 6	MCP, 8404	270, 8	1.4	1.6
17	ICA, 849	810, 6	MCP, 8404	290, 4	4.0	0.8
18	MCP, HR/321	800, 6	JM, 70168	300, 3	12.5	0.4
19	MCP, HR/321	800, 6	MCP, 8404	300, 3	0.9	2.3
20	MCP, HR/321	800, 6	MCP, 8404	325, 3	3.5	0.9
21	MCP, HR/321	800, 6	MCP, 8405	320, 3	4.0	3.5
22	UMC, 8426	800, 6	MCP, 8405	310, 3	6.5	0.7

Material source:

ICA - Indium Corporation of America

JM - Johnson Matthey

MCP - MCP Ltd.

RASA - RASA Industries

UMC - United Mineral and Chemical

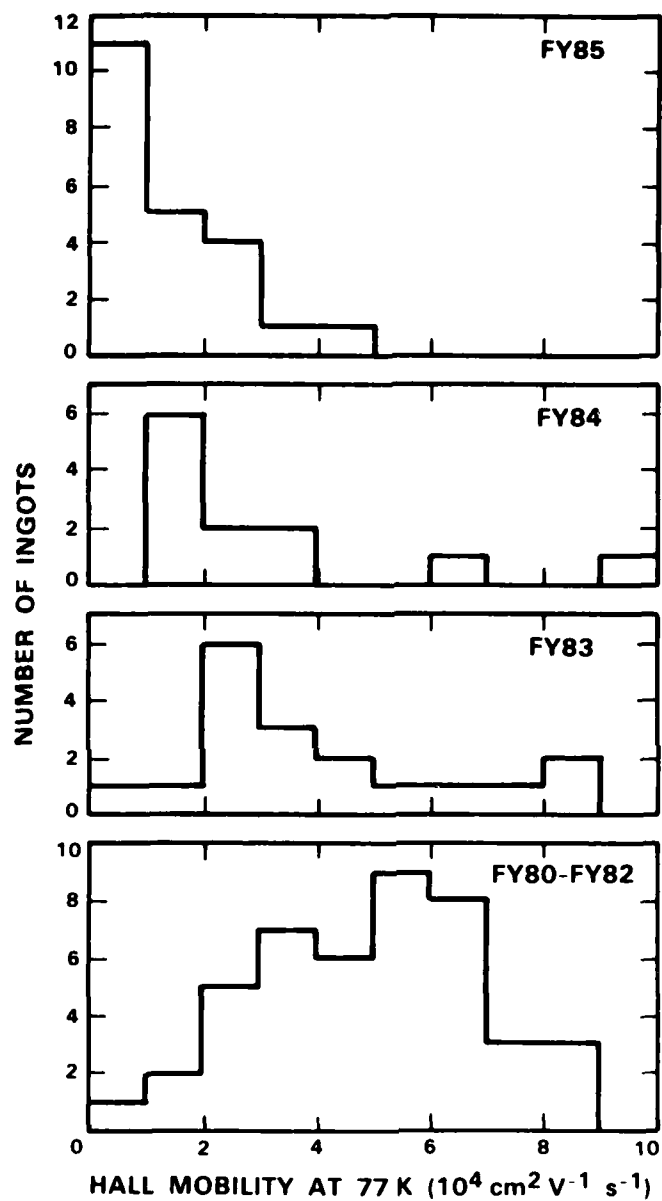


Figure 1. Distribution of electron Hall mobilities at 77 K for polycrystalline InP ingots.

reduction in yield to a combination of two factors: the continuing low purity of as-received P relative to the purity of FY80-82 material and a decrease in the effectiveness with which electrically active impurities were removed (or rendered inactive) by P prebaking. We believe that these two factors also caused the additional reduction in yield during FY85.

In last year's report we noted that Si was the principal impurity found by SIMS analysis in the polycrystalline InP ingots. Evidence that Si was still the dominant impurity during FY85 is obtained by comparing the carrier concentrations in the five nominally undoped LEC InP boules grown in FY85 with the concentrations in the ingots that provided charges for these boules. The two sets of carrier concentrations, which approximate the shallow donor concentrations, and the corresponding carrier mobilities are listed in Table II. Similar data are listed for the three nominally undoped boules grown in FY80. For each of the FY85 boules the carrier concentration is much lower than the concentration in the charge material. (In fact, the values for boules 664 and 676 are comparable to those for the FY80 boules, although the concentrations in the charge material were an order of magnitude higher.) If the reduction in concentration had occurred because the dominant impurity was a donor with a distribution coefficient significantly less than one, such as Ge or Sn, the concentration would increase systematically along the length of the boule. However, this is not the case. Even for boules 688 and 726, in which the carrier concentrations are much higher than the normal background of $2-4 \times 10^{15} \text{ cm}^{-3}$, there is little change in concentration with

Table II. Electrical Properties of Nominally Undoped EC InP Crystal

FY	Number	LEC Boule		Number	Starting Charge	
		$(10^{16} \text{ cm}^{-3})$	$(10^{16} \text{ cm}^{-3})$		$(10^{16} \text{ cm}^{-3})$	$(10^{16} \text{ cm}^{-3})$
80	268	0.28	4.1	80-1	0.12	8.3
	280	0.30	3.5	80-2	0.10	3.9
	294	0.40	3.4	80-3	0.08	7.2
85	664	0.36	3.2	85-5	1.0	2.2
	676	0.47	3.0	85-8	6.3	0.62
	680	0.86	2.2	85-9	5.7	0.63
	688	1.1	2.0	85-7 (60%) 85-12 (40%)	9.9 1.9	0.50 1.0
	726	4.0	0.9	----	-5*	< 0.6

*Estimated from $\rho_{300} / \rho_{77} \approx 1.4$

distance. The concentration reduction can therefore be attributed to gettering of the dominant impurity from the melt by the B_2O_3 encapsulating layer. Since Si is the only donor that we know to be effectively gettered by B_2O_3 , we conclude that Si is the dominant impurity.

With the objective of increasing the purity of the InP ingots, we have recently acquired high-purity In and P from new sources, but we have not yet performed any synthesis runs with these elements. We have also recently acquired high-purity In_2O_3 for the purpose of preparing oxide-doped melts in an attempt to getter Si by the formation of SiO_2 and thereby suppress its incorporation into the InP ingots.

LEC GROWTH IN THE $\langle 100 \rangle$ ORIENTATION

For almost all the LEC InP boules grown in previous years the growth axis was in a $\langle 111 \rangle$ direction. The (100) slices cut from such boules to provide substrates for epitaxial growth and device fabrication are oval in shape. Since circular substrates are preferred for these applications, we have begun to investigate LEC growth in the $\langle 100 \rangle$ direction. Twenty-one boules, either undoped or doped with Fe, Sn, or Zn, have been grown to date from $\langle 100 \rangle$ seeds. With a few exceptions, each run employed the same growth conditions that had produced a twin-free [111B] single-crystal boule in the previous run. Only two of the 21 runs yielded untwinned single-crystal $\langle 100 \rangle$ boules. Several other boules consisted mainly of a $\langle 221 \rangle$ single crystal that originated when an unnoticed twin boundary crossed the boule early in the run, but the remaining boules were very

polycrystalline as a result of twinning. In this series of paired $\langle 100 \rangle$ and $[111\text{B}]$ runs, which used a fairly wide range of growth conditions (including various values of B_2O_3 encapsulant thickness, crucible and susceptor heights, seed and crucible rotation rates, and argon gas pressure, as well as both as-synthesized, In-rich polycrystalline charge material and pre-pulled, more nearly stoichiometric charges), twinning was much more probable for $\langle 100 \rangle$ growth than for $[111\text{B}]$ growth. Further experiments are planned to test the effect of the B_2O_3 water content and the source of the B_2O_3 material on the twinning probability in $\langle 100 \rangle$ growth. To obtain a yield of twin-free $\langle 100 \rangle$ single crystals comparable to the yield of such $\langle 111 \rangle$ crystals, it apparently will be necessary to use higher temperature gradients during LEC growth. Although increasing the gradients tends to increase the dislocation density, for one of the twin-free $\langle 100 \rangle$ boules this density was reasonably low for the size of the boule. Near the bottom of this boule, which was grown from a nominally undoped charge in a PBN crucible with a two-piece susceptor as described in the FY84 report, the etch pit density varied from $\sim 10^4$ to $\sim 10^5$ cm^{-2} across the diameter of 49 mm.

CHARACTERIZATION OF Fe-DOPED InP

In anticipation of a proposed Lincoln Laboratory research program on millimeter-wave and microwave devices fabricated on InP substrates, which will include a study of the correlation between device characteristics and substrate properties, we have begun an effort to improve the

characterization of our Fe-doped semi-insulating LEC boules. In particular, we are developing a technique for obtaining better estimates of the residual donor impurity concentration, which may have a very important effect on ion-implanted device structures. For this purpose we are utilizing low-temperature measurements of the optical absorption in the vicinity of 3.5 μ m that is associated with intra-atomic transitions from the ground state of the $\text{Fe}^{2+}(3d^6)$ levels.¹ Since these levels are obtained by transfer of electrons from donors to the unoccupied Fe^{3+} deep acceptors, in semi-insulating samples the Fe^{+2} concentration is equal to the net shallow donor concentration, the excess of shallow donors over shallow acceptors.

In the vicinity of liquid helium temperature, where the Fe^{2+} levels are nearly all in the ground state, the Fe^{2+} concentration for any sample is given by the measured absorption coefficient divided by the absorption cross section. In order to determine this cross section we are using a technique that we have developed for adding Fe to the melt after an initial portion of the crystal has been grown. From the results of Hall coefficient and resistivity measurements, we can obtain the net shallow donor concentration in the material grown just before Fe doping. For the cross section determination the original melt is doped with a shallow donor at a concentration such that the concentration incorporated in the crystal is small enough to be completely compensated by the Fe that is added subsequently, but high compared to the concentration of shallow donors that may be unintentionally added along with the Fe. In this case

the net shallow donor concentration is essentially the same in the portions of the boule grown just before and after Fe doping, and the absorption cross section is given by the ratio of the absorption coefficient for the latter portion to the carrier concentration for the former. (If the original melt is not doped, the Hall coefficient measurements will yield the net shallow donor concentration in the nominally undoped material grown before Fe doping. In general this concentration will differ significantly from the residual impurity concentrations in samples from the Fe-doped portion of the boule. As noted previously,² the concentrations of shallow impurities introduced along with the Fe are significant compared to the concentrations of such impurities in nominally undoped material. In addition, the residual impurities have distribution coefficients much less than unity and therefore vary in concentration along the length of the boule.)

In initial experiments to investigate the new technique, measurements of the 3.5 μm absorption band have been made on several Fe-doped semi-insulating samples at a temperature estimated to be below 15 K. For one sample cut from the region of a boule grown just after Fe doping, the peak absorption coefficient (α) was 0.45 cm^{-1} . The carrier concentration measured for a sample from the region grown just before Fe doping was $4 \times 10^{16} \text{ cm}^{-3}$, giving an Fe^{2+} absorption cross section of $1.1 \times 10^{-17} \text{ cm}^2$. For two semi-insulating samples from boules that had been grown from Fe-doped charges, the measured values of α were 0.18 and 0.55 cm^{-1} . Using the measured cross section we obtain net shallow donor concentrations of

1.6×10^{16} and $5.0 \times 10^{16} \text{ cm}^{-3}$, respectively. We plan to perform additional experiments to check the cross section value, and then will use the absorption technique for routine characterization of semi-insulating substrates.

OPTICAL AND ELECTRICAL PROPERTIES OF V-DOPED InP

Semi-insulating bulk InP crystals have so far been prepared only by doping with Fe or Cr, which typically yield resistivities of 10^7 - 10^8 and 10^4 - $10^5 \Omega \text{ cm}$, respectively. The thermal stability of substrates obtained from such crystals is marginal. Since the preparation of semi-insulating GaAs by means of V doping has recently been reported,^{3,4} we have carried out an investigation to determine whether V doping can also be used to prepare semi-insulating InP. Our results support the conclusion of Bremond, et al.⁵ that V in InP is a donor located close to the valence band. Therefore semi-insulating InP cannot be prepared by doping with V.

To obtain V-doped samples for optical and electrical measurements, a number of [111B] LEC boules were grown from melts containing 0.3 to 0.6 at.% V. In some growth runs V metal was added to the starting charge. In others, in order to demonstrate the effects of V doping as clearly as possible, the V was dropped into the melt after part of the boule had been grown, and samples were cut from the regions grown before and after the V was added. This delayed doping procedure was employed in growing one n-type boule and several p-type boules, using starting charges that were nominally undoped and lightly Zn-doped, respectively. For Hall

coefficient measurements, samples about $1 \times 4 \times 30 \text{ mm}^3$ were prepared with their long dimension parallel to the [111B] growth axis. Current leads were soldered to the ends of each sample, and pairs of leads were soldered across from one another on the smaller side faces at intervals of about 3 to 5 mm along the length. A Hall coefficient measurement was then made at room temperature with each pair of transverse leads. For optical measurements, longitudinal (110) slabs about 1 cm thick were cut and polished, and the transmission was measured at several locations along the length.

Electrical measurements were made on samples from each of the V-doped boules. For the boules pulled from melts that were nominally doped only with V, the samples were n-type with carrier concentrations in the 10^{15} to 10^{16} cm^{-3} range. For the n-type boule grown by the delayed doping procedure, the results of Hall coefficient measurements made as a function of distance along the vertical axis are shown in Fig. 2. The electron concentration increases from less than $2 \times 10^{15} \text{ cm}^{-3}$ to about $3 \times 10^{15} \text{ cm}^{-3}$ just after the melt was doped with -0.5 at.% V and finally to nearly $7 \times 10^{15} \text{ cm}^{-3}$ near the last-to-freeze part of the boule. No sharp discontinuity in the carrier concentration is observed.

All of the boules pulled from melts doped with Zn were p-type, both before and after V was added to the melt. No semi-insulating behavior was observed for any V-doped crystals. Figure 3 shows the free hole concentration (e/R_H) versus distance along the growth axis of a boule pulled from a melt initially doped with Zn and later additionally doped with

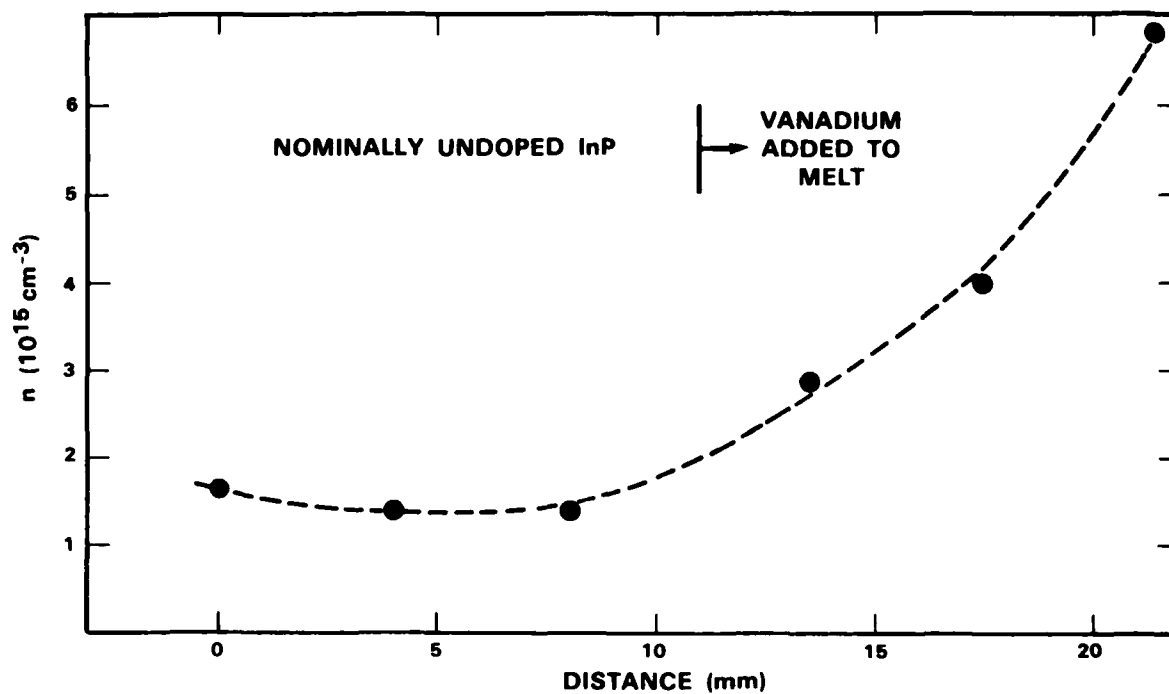


Figure 2. Carrier concentration vs distance along the vertical axis for an n-type InP boule initially grown without intentional doping and then doped with V.

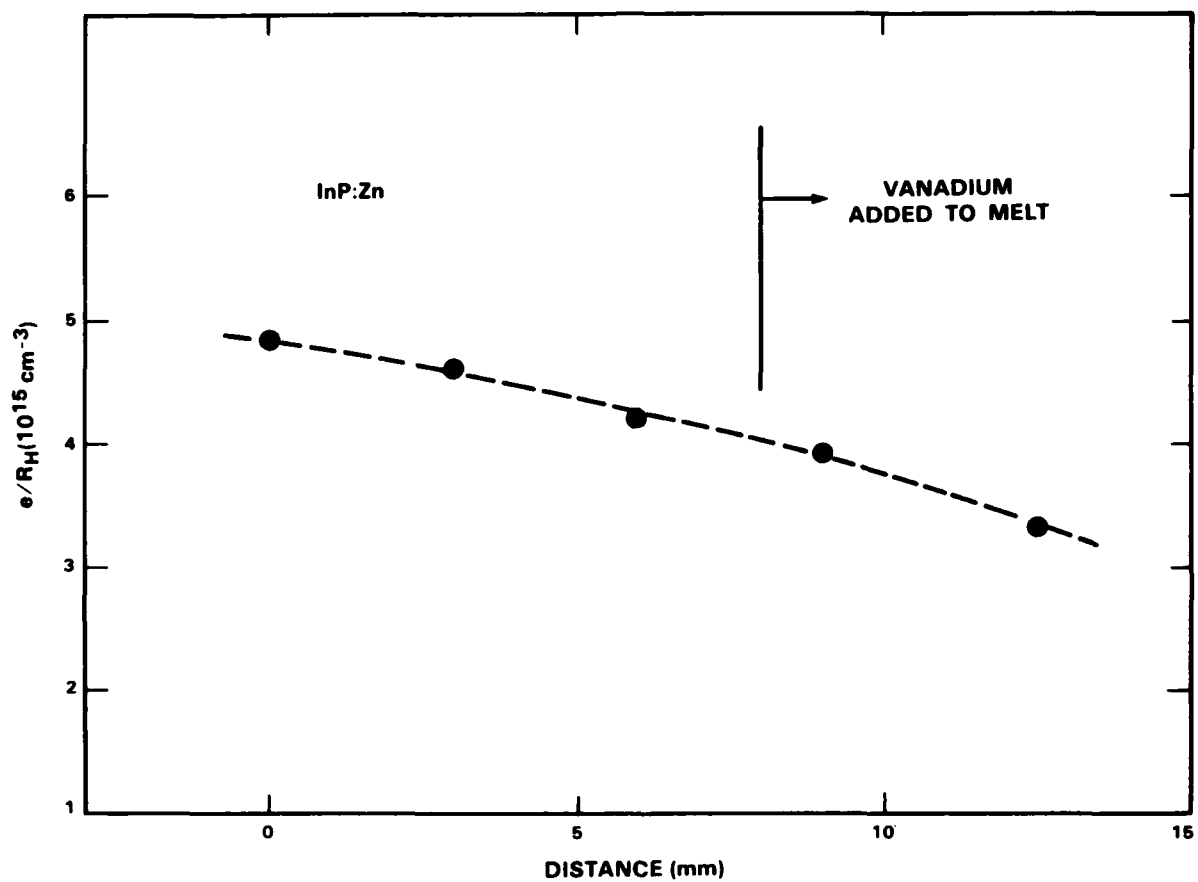


Figure 3. Carrier concentration vs distance along the vertical axis for a p-type InP boule initially doped with Zn and then additionally doped with V.

-0.4 at.% V. In this case the carrier concentration decreases slowly from about 5×10^{15} to $3 \times 10^{15} \text{ cm}^{-3}$, again with no discontinuity at the point where V was added.

Measurements of the Hall coefficient were made as a function of temperature for a Zn-doped sample and for a sample doped with both Zn and V. The results are shown in Fig. 4, where the log of R_H is plotted versus reciprocal absolute temperature. Because the electrical contacts were non-ohmic on these lightly doped p-type samples, the data are scattered, but they indicate a significant difference in the activation energy, which is about 0.03 eV for the Zn-doped sample and 0.1 eV for the V,Zn-doped sample.

The optical absorption spectra at 77 and 300 K for a V-doped n-type sample with carrier concentration of $4 \times 10^{15} \text{ cm}^{-3}$ are shown in Fig. 5 for wavelengths between 0.9 and 1.6 μm . Three peaks appear in the 300 K spectrum between 1.05 and 1.3 μm , but they are relatively broad and not well resolved. At 77 K, five peaks are observed. However, since they are not significantly narrower than those at 300 K, there is no advantage in obtaining 77 K data. Figure 6 shows absorption spectra for samples from the top and bottom of the p-type boule from which the hole concentration data of Fig. 3 were obtained. These spectra clearly indicate the effect of V on the absorption in the region of the intrinsic absorption edge. The absorption in the sample from the bottom of the boule, which was doped with both V and Zn, is similar but not identical to the spectrum shown in Fig. 5 for the n-type sample. The V absorption

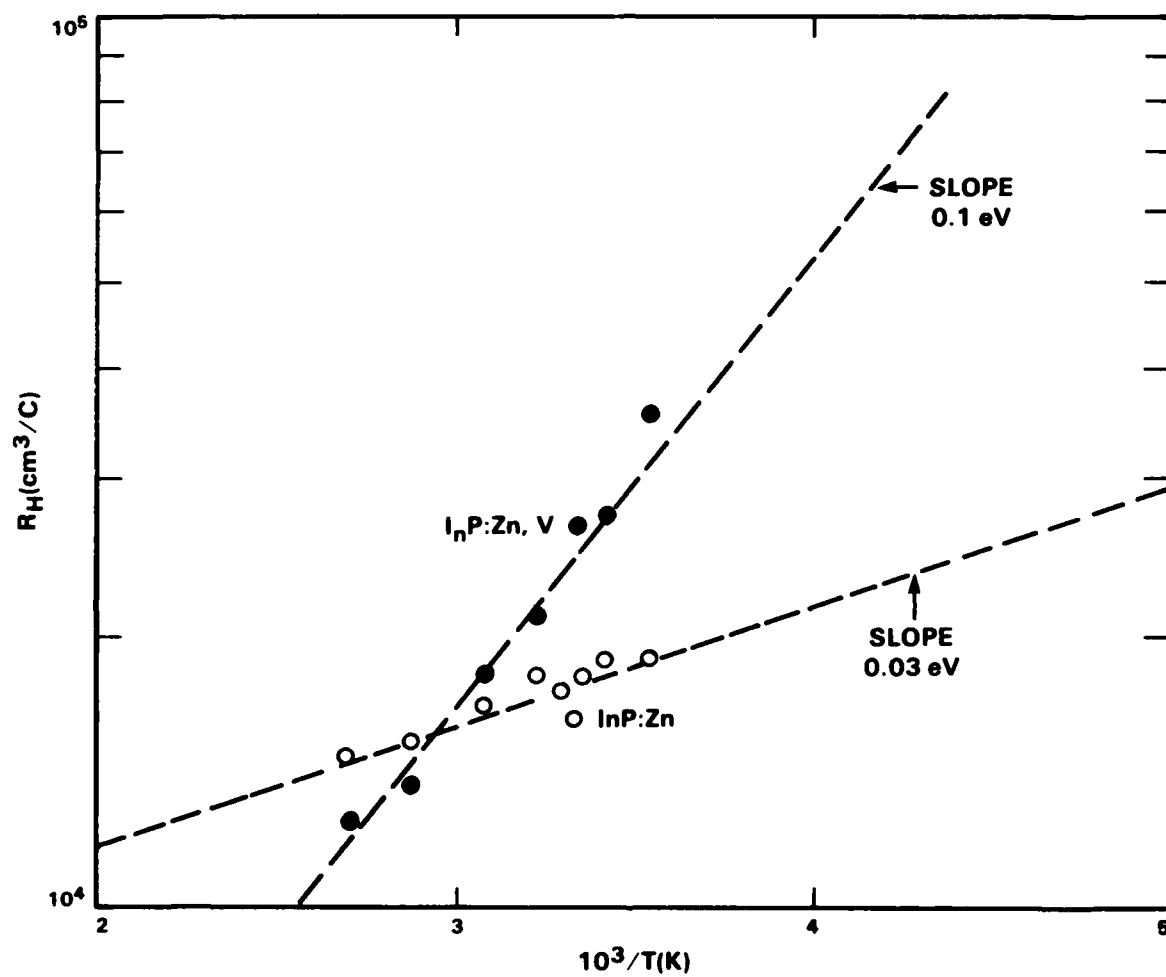


Figure 4. Hall coefficient vs reciprocal absolute temperature for Zn- and Zn,V-doped InP samples.

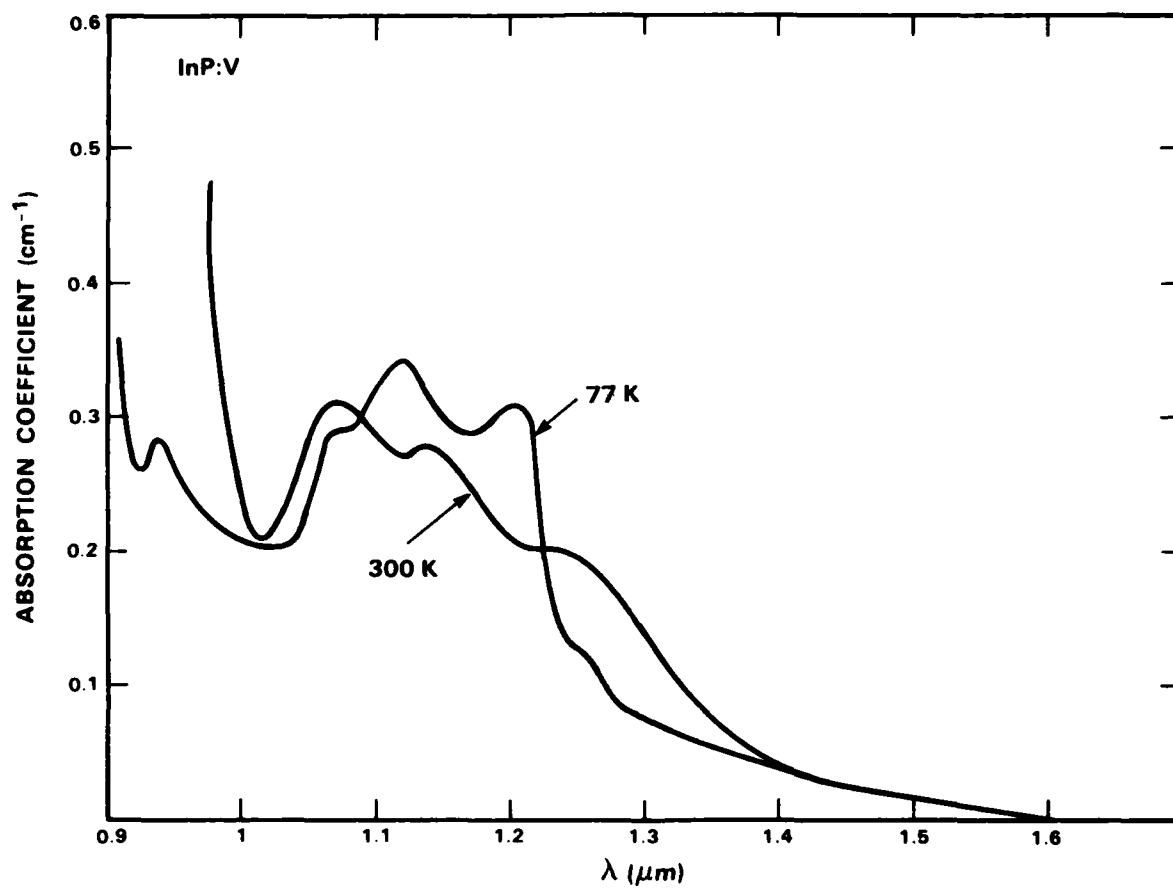


Figure 5. Optical absorption vs wavelength for an n-type InP sample doped with V but not intentionally doped with any other impurity.

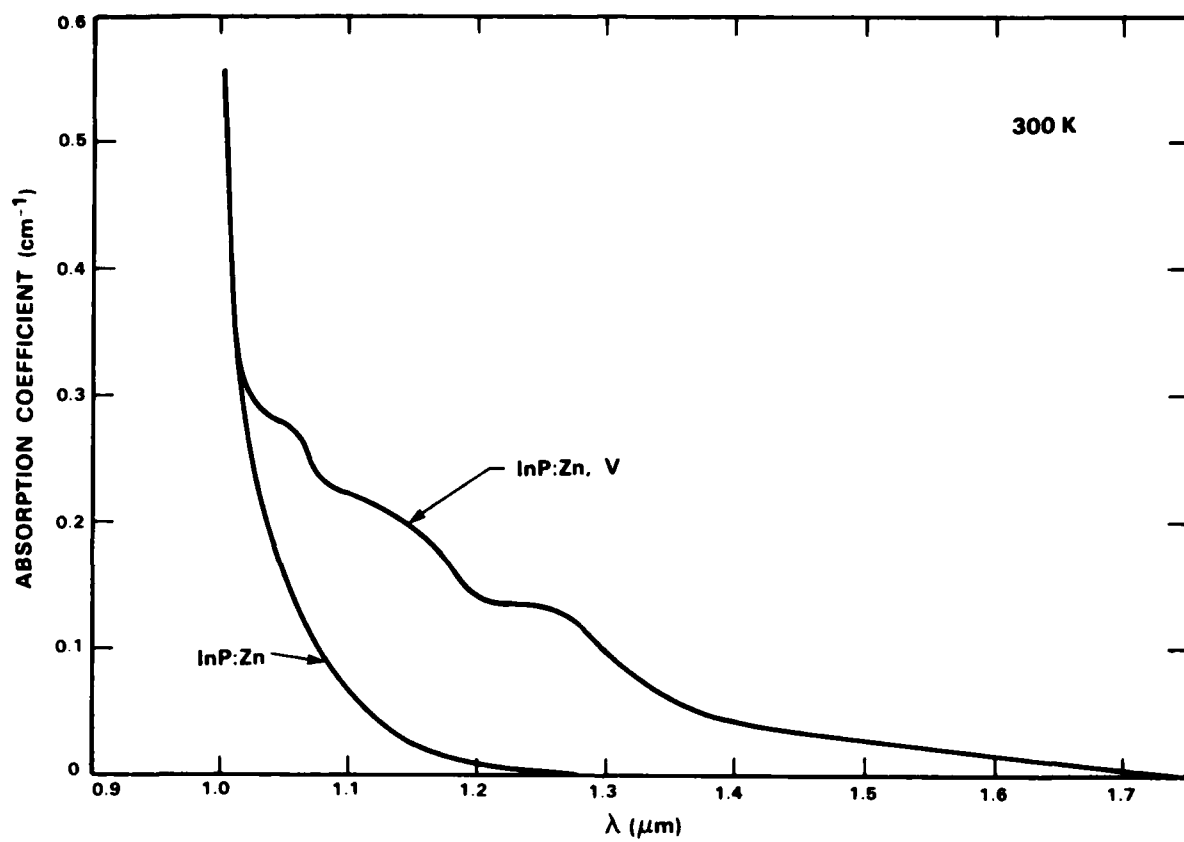


Figure 6. Optical absorption vs wavelength for regions of a Zn-doped, p-type InP boule grown before and after addition of V to the melt.

bands are somewhat distorted in the p-type material because the absorption edge is shifted to longer wavelengths.

The solid curve in Fig. 7 shows the optical transmission spectrum measured at 300 K for an 8-mm-thick p-type sample with approximately the same V concentration as the V,Zn-doped sample of Fig. 6 but a considerably higher Zn concentration. The hole concentration of the sample of Fig. 7 is $2.4 \times 10^{17} \text{ cm}^{-3}$, so that the free carrier optical absorption strongly reduces the transmission, even for wavelengths near the absorption edge. The measured spectrum does not exhibit the characteristic V structure observed for the sample of Fig. 6. The absence of this structure indicates that the V centers in the sample of Fig. 7 are in a different electronic state that does not yield the structured absorption. If this absorption had occurred, the spectrum would have approximated the dashed spectrum in Fig. 7, which shows that the structure would have been observed in spite of the strong background of free carrier absorption. To obtain the dashed spectrum, a curve of α vs λ was calculated from the measured transmission curve. To take account of the hypothetical V absorption, an adjusted α - λ curve was then obtained by adding the difference between the absorption spectra for the V,Zn- and Zn-doped samples of Fig. 6. The adjusted α - λ curve was then used to calculate the dashed transmission spectrum.

Our electrical and optical data for InP:V are consistent with the model proposed by Bremond, et al.⁵ On the basis of deep-level optical spectroscopy and secondary-ion mass spectrometry (SIMS) data, these authors have concluded that V in InP is a very deep donor that is located

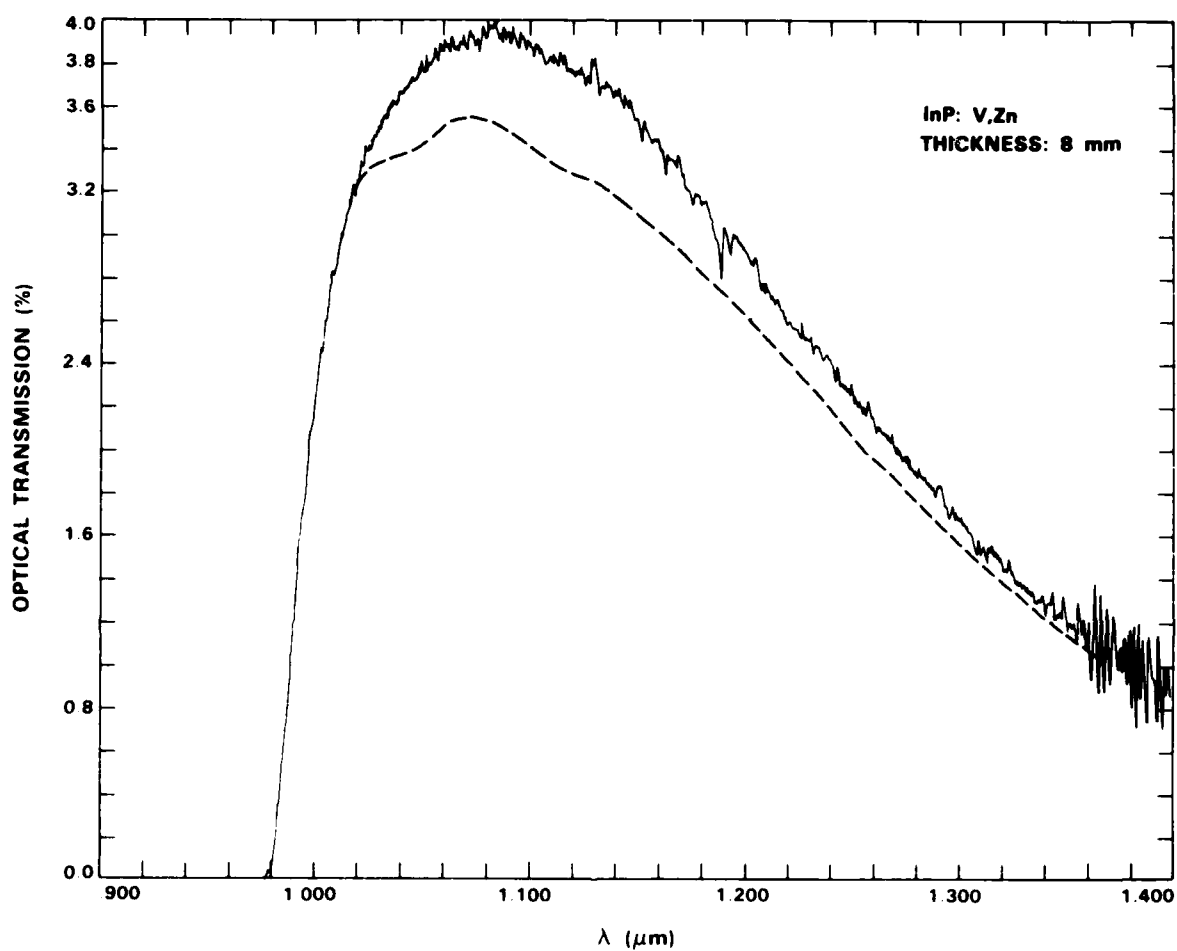


Figure 7. Optical transmission vs wavelength measured for V,Zn-doped InP sample (solid line) and calculated for the same sample by assuming intra-atomic absorption due to V (dashed line).

only about 0.2 eV above the valence band edge and has a solubility concentration in the mid 10^{15} cm^{-3} range.

For p-type InP:V co-doped with a shallow acceptor, according to Bremond's model the equilibrium carrier concentration and occupation of the V donor level are given by the following equations:

$$p N_d^0 \approx N_d^+ N_v \exp(-E_d^+/kT)$$

$$p = N_A - N_d^+$$

$$N_d^0 = N_d - N_d^+ = N_d - N_A + p$$

where p is the hole concentration, N_d^0 the concentration of neutral V, N_d^+ the concentration of ionized V, N_v the valence band density of states, E_d^+ the energy difference between the V donor level and the valence band, N_A the net shallow acceptor concentration, and N_D the total V concentration. For $N_d \approx N_A$,

$$p \approx (N_A - p)N_v \exp(E_d^+/2kT),$$

so that the slope of a plot of the log of the Hall coefficient versus reciprocal temperature is approximately one-half E_d^+ . The preliminary data shown in Fig. 4 indicate an activation energy of -0.1 eV, consistent with Bremond's value of -0.2 eV for E_d^+ . Further

measurements over a greater temperature range will be necessary to obtain an accurate value for E_d' .

The data in Fig. 3, which show that the hole concentration in a Zn-doped boule decreased gradually rather than abruptly when V was added to the melt, are consistent with the model of V as a donor with $E_d' \approx 0.2$ eV. The Fermi level in this boule, for which p is $3-5 \times 10^{15} \text{ cm}^{-3}$, is located at about the same energy as the V level. Therefore V donors would be less than 50% effective in reducing the hole concentration. Since the solubility of V in InP is reported by Bremond et al. to be in the mid 10^{15} cm^{-3} range, not much change in hole concentration would occur even if the concentration of V incorporated into the boule were equal to the solubility.

According to the deep donor model for V, there should be no change in carrier concentration when V is incorporated in an n-type InP boule. Figure 2 shows a gradual increase in carrier concentration after V was added to a nominally undoped melt, but this increase can be attributed to the segregation of residual impurities frequently observed in growth from such melts, the introduction of a shallow donor as a contaminant in the V, or a change produced by V in the gettering action of the B_2O_3 encapsulant.⁶

Our optical absorption data strongly support the deep donor model for V in InP. The structured absorption shown in Figs. 5 and 6 has previously been observed in n-type InP:V by Zakharenkov, et al.,⁷ who attributed it to intra-atomic transitions of the V center. Mircea-Roussel, Martin, and

Lowther⁸ have attributed a nearly identical absorption spectrum in semi-insulating GaAs:V to excitation of the $V^{3+}(3d^2)$ ground state. Since the crystal field splitting of V is expected to be very similar in GaAs and InP, we assume that the configuration responsible for the intra-atomic V absorption in InP is also $V^{3+}(3d^2)$. This is the configuration for an un-ionized V center that is substituted for the Group III element in a III-V compound. If the center is a donor, as in InP, it will remain un-ionized as long as its energy level is located significantly below the Fermi level. This is the case for the n-type sample of Fig. 5 and the lightly Zn-doped p-type sample of Fig. 6. Consequently these samples exhibit the characteristic intra-atomic absorption associated with $V^{3+}(3d^2)$. For the p-type sample of Fig. 7, however, the carrier concentration is $2.4 \times 10^{17} \text{ cm}^{-3}$, placing the Fermi level only about 0.08 eV above the valence band. Since the V donor is located about 0.2 eV above the valence band, it will be ionized by loss of an electron, changing its configuration to $V^{4+}(3d^1)$, which does not exhibit intra-atomic absorption in the 1-1.3 μm wavelength range.

Recently Brandt, et al.⁹ have reported that V in GaAs is a very deep acceptor located about 0.15 eV below the conduction band edge. This center will remain un-ionized, and therefore in the $V^{3+}(3d^2)$ configuration, only if its energy level is located above the Fermi level. Consequently the intra-atomic V absorption is observed for semi-insulating samples, but not for n-type samples, in which the center accepts an electron to become $V^{2+}(3d^3)$. It is curious that V acts as a donor in InP

and as an acceptor in GaAs. In each case a very large fraction of the bandgap energy is required to ionize the center. That $V^{3+}(3d^2)$ is more easily ionized in InP by removing an electron and in GaAs by adding an electron is perhaps related to the stronger ionic nature of the bonding in InP. Caldas, Fazzio, and Zunger¹⁰ have recently reported general trends in the binding energies of deep impurities in compound semiconductors by referring the energies to the vacuum level. They predicted that V in GaAs would be an acceptor in the upper third of the bandgap, as subsequently confirmed by Brandt, et al.⁹ They predicted that V in InP would be an even deeper acceptor, with its energy level degenerate with the conduction band. They did not consider the possibility that a center requiring so much energy for ionization by accepting an electron might be more easily ionized by losing an electron, thus behaving as a donor rather than an acceptor.

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UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ESD-TR-85-316	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) InP Materials		5. TYPE OF REPORT & PERIOD COVERED Annual Technical Summary 1 Oct. 1984 — 30 Sept. 1985
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Gerald W. Iseler		8. CONTRACT OR GRANT NUMBER(s) F19628-85-C-0002
9. PERFORMING ORGANIZATION NAME AND ADDRESS Lincoln Laboratory, M.I.T. P.O. Box 73 Lexington, MA 02173-0073		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Program Element No. 61102F Project No. 2306
11. CONTROLLING OFFICE NAME AND ADDRESS Rome Air Development Center Griffiss AFB, NY 13440		12. REPORT DATE 30 September 1985
		13. NUMBER OF PAGES 32
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Electronic Systems Division Hanscom AFB, MA 01731		15. SECURITY CLASS. (of this Report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES None		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Liquid growth, InP synthesis, InP crystal growth, Czochralski (LEC), single crystals, stability		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report covers the work on InP materials carried out with the support of the Department of the Air Force during the period 1 October 1984 through 30 September 1985. A part of this support was provided by the Rome Air Development Center. The probability of twinning in LEC growth of InP was found to be much higher for the <100> orientation than for the <111>. An optical absorption technique is being developed for estimating the residual impurity concentration in semi-insulating Fe-doped InP. It has been shown that V in InP behaves as a deep donor located ~0.2 eV above the valence band.		

END